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Reid, Joshua Elias Samuel James, Bernardes, Carlos E S, Agapito, Filipe et al. (4 more authors) (2017) Structure-property relationships in protic ionic liquids : a study of solvent-solvent and solvent-solute Interactions. Physical Chemistry Chemical Physics. pp. 28133-28138. ISSN 1463-9084

https://doi.org/10.1039/c7cp05076c

Journal Name

ARTICLE

Structure-Property Relationships in Protic Ionic Liquids: A Study of Solvent-Solvent and Solvent-Solute Interactions

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The ionic nature of a functionalized protic ionic liquid cannot be rationalized simply through the differences in aqueous proton dissociation constants between the acid precursor and the conjugate acid of the base precursor. The extent of proton transfer, i.e. the equilibrium ionicity, of a tertiary ammonium acetate protic ionic liquid can be significantly increased by introducing an hydroxyl functional group on the cation, compared to the alkyl or amino-functionalized analogues. This increase in apparent ionic nature correlates well with variations in solvent-solute and solvent-solvent interaction parameters, as well as with physicochemical properties such as viscosity.

1 Introduction

Protic ionic liquids (PILs), formed by proton transfer from a Brønsted acid (AH) to an appropriate base (B) to produce the ionic species [HB][A], offer a promising opportunity to expand the range of solvents available for physical, chemical, and biological processes.[1,2] Their ease of preparation, without solvents, work up or further ion-exchange reactions, makes them an attractive alternative to aprotic ionic liquids (AILs),[3] as do the comparatively "green" credentials such as low toxicity, ready biodegradability, and non-mutagenicity, exhibited by many PILs, notably ammonium carboxylates.[4,5] The potential for the use of PILs as solvents has been shown in a range of applications including natural product extraction,[6] biomass processing,[7] fuel processing,[8] biocatalysis,[9] and CO_2 capture.[10]

The extent to which a PIL may be considered "ionic" can vary considerably depending on the structures of the component ions. In some cases, the extent of proton transfer of a PIL has been shown to correlate with the differences in aqueous proton dissociation constants (ΔpK_a) between the acid precursor (HA) and the conjugate acid of the base precursor, $[HB]^+$, which corresponds to the cationic moiety.[11] We clarify here that the extent of proton transfer within a PIL is a measure of its equilibrium ionicity,[12–17] which is fundamentally different from the dynamic ionicity reflected by the ion mobility commonly inferred from Walden plots.[11,18,19] The relation of ΔpK_a to the equilibrium ionicity, while valid for many PILs,[19] is inadequate for accurately predicting the ionic nature of all members of the class. Indeed, it has previously been shown that primary and tertiary ammonium carboxylate PILs can exhibit significantly different apparent ionicities, despite having similar ΔpK_a values.[20]

Recently, various spectroscopic techniques have been employed to study the extent of proton transfer in PILs. For PILs with carboxylate anions, the infrared (IR) spectra can give insights into vibration modes corresponding to the neutral and ionic species present in the system. Specifically, for an ammonium carboxylate PIL one can observe the asymmetric stretching vibration of the COO^- functional group of the anionic species at around 1570 cm^{-1} and the C=O stretching vibration of the neutral species at around 1710 cm^{-1}.[15,17] Another important source of information has been NMR spectroscopy. The deshielding of the amine nitrogen center in ^{15}N NMR spectra, has, for example, been suggested to reflect the extent of proton transfer.[21] Utilising ^1H NMR, where quantitative analysis is more feasible, attempts have also been made to quantify the extent of proton transfer solely from spectroscopic measurements.[17,22,23]

While multiple PILs have been studied, there has been little exploration into how additional functional groups with hydrogen bonding ability, such as hydroxyl (HO-) or dimethylamino (Me_2N-), can influence the extent of proton transfer. There is, in addition, a poor understanding of how the extent of proton transfer impacts on the solvation properties of PILs. Uncovering relationships between equilibrium ionicity and molecular structure is therefore of considerable interest to the design of PILs with task specific solvent properties.

Here we report a study of the equilibrium ionicity in three tertiary ammonium carboxylate PILs by attenuated total reflectance infrared (ATR-IR) and ^1H NMR spectroscopy. The three PILs feature the common acetate anion, with varying cation functionality (Fig. 1): *N,N*-dimethylbutylammonium acetate, [HDMBuA][OAc] (**1**); 2-(dimethylamino)-*N,N*-dimethylethylammonium acetate, [HTMEDA][OAc] (**2**); and

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Electronic Supplementary Information (ESI) available: [Synthesis and characterization procedure and information on ATR-IR, solvatochromic parameters, density and viscosity for protic ionic liquids]. See DOI: 10.1039/x0xx00000x

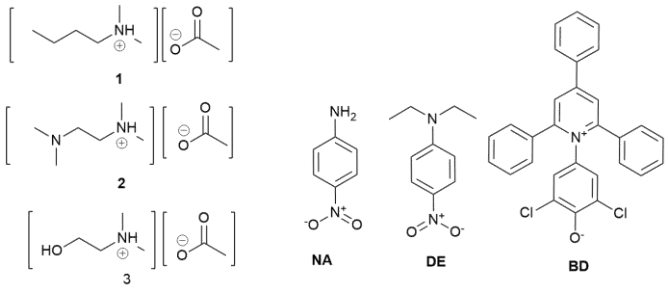

Fig. 1: Molecular structures of the PILs and of the solvatochromic probes used in this study.

N,N-dimethylethanolammonium acetate, [HDMEtA][OAc] (**3**). ~~The~~ PILs **1**, **2** and **3** (Fig. 1) have relatively similar ΔpK_a values of 5.26, 4.38 and 4.87,[24–27] respectively, and from the referred established relation should have comparable equilibrium ionicity.[18] The insight into the equilibrium ionicity from spectroscopic methods will form the basis to rationalize the connection between the extent of proton transfer in a PIL and its properties as a solvent.

Solvation behavior depends on both solvent-solute and solvent-solvent interactions. These multiple contributions to solvation can be considered independently from one another and characterized through experimentally determined parameters such as those outlined by Kamlet and Taft.[28] Specific solvent-solute interactions i.e. hydrogen bond donor acidity (α) and hydrogen bond acceptor basicity (β), as well as non-specific solvent-solute interactions such as dipolarity/polarizability (π^*), can be evaluated by using selected solvatochromic probes (Fig. 1). While the best practice for accurately obtaining α, β, and π^* is by using multiple solvatochromic probes per parameter,[29,30] there are limited datasets in the literature for cross comparison, and none known to the authors for PILs. Three solvatochromic probes were therefore selected in this work to determine α, β, and π^*: 4-nitroaniline (NA), *N,N*-diethyl-4-nitroaniline (DE), and 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (BD) (Fig. 1).[28,31–35] The net contribution of solvent-solvent interactions to solvation, also considered by Kamlet and Taft,[28] was weighted by the Hildebrand solubility parameter (δ_H), which is calculated from cohesive energy density values (CED, see below).[36] Using these parameters, it is possible to quantify how specific and non-specific solvent-solute and net solvent-solvent interactions correlate with the ionic nature of a tertiary ammonium acetate PIL.[28,36–38] Finally, the bulk viscosity of each PIL was also experimentally measured to investigate how the variation of PIL cation structure influences this important physicochemical property.

2 Materials and methods

2.1 General

All PIL precursor materials, namely *N,N*-dimethylbutylamine (DMBuA), ≥99.0%, *N,N,N′,N′*-tetramethylethane-1,2-diamine (TMEDA), ≥99.5%, *N,N*-dimethylethanolamine (DMEtA), ≥99.5%, acetic acid (HOAc), ≥99.5%, and the solvatochromic dyes (Fig. 1) 4-nitroaniline (NA), ≥99.0%, and 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (BD), ≥97.0%, were supplied from Sigma Aldrich UK. The dye *N,N*-diethyl-4-nitroaniline (DE), 97%, was supplied from Fluorochem UK. All these materials were used without further purification.

The method used in the preparation of compounds **1**, **2** and **3** has been previously detailed.[3,39] In brief, a flask purged with N_2 was charged with the precursor amine and placed in an ice bath. Acetic acid was added to the flask dropwise while stirring. After complete addition, the reaction was left to stir for 24 h, to ensure that proton exchange had been brought to equilibrium.

Because of the known effects of water on the liquid structure of PILs,[40–43] the water content of **1**, **2**, and **3** was measured by Karl-Fischer titration and found to vary between 645 ppm and 1057 ppm. At these concentrations, the effect of water on the total PIL-PIL interactions is negligible.[40–43]

*Synthesis of [HDMBuA][OAc] (**1**).* Mass of DMBuA: 5.1158 g (50.6 mmol), mass acetic acid: 3.0961 g, (51.6 mmol). Molar percentages of components as determined from the above masses: 50.5% (acid), 49.5% (amine). Water content from Karl Fischer titration: 645 ppm.

*Synthesis of [HTMEDA][OAc] (**2**).* Mass TMEDA: 4.6541 g (40.1 mmol), mass acetic acid: 2.4377 g (40.6 mmol). Molar percentages of components as determined from the above masses: 50.3% (acid), 49.7% (amine). Water content from Karl Fischer titration: 1057 ppm.

*Synthesis of [HDMEtA][OAc] (**3**).* Mass DMEtA: 4.4747 g (50.2 mmol), mass acetic acid: 3.0404 g (50.6 mmol). Molar percentages of components as determined from the above masses: 50.2% (acid), 49.8% (amine). Water content from Karl Fischer titration: 900 ppm.

2.2 Attenuated Total Reflectance Infrared (ATR-IR) spectroscopy

The ATR-IR spectra of all precursor materials and protic ionic liquids were recorded at room temperature using an A_2 Technologies (Agilent) ExoScan Fourier-Transform Infrared Spectrometer fitted with a Germanium crystal attenuated total reflectance interface. All measurements were performed between 3500 cm^{-1} and 800 cm^{-1}. A background signal was recorded 32 times to produce a single averaged background spectrum. The sample was then placed directly on to the interface for immediate measurement of 32 scans and then averaged to produce a single sample spectrum. The interface was cleaned using a dry paper towel and propan-2-ol. Once the interface was sufficiently clean to return the beam to the background baseline, the instrument was ready for subsequent measurements. Each sample was recorded three times for a total of 96 scans and the obtained data averaged to produce the final infrared spectrum.

2.3 NMR Spectroscopy

^1H and ^{13}C NMR analysis of the pure PILs were performed using a Bruker 700 MHz NMR instrument.[21] A Wilmad coaxial inset contained a solution of D_2O with 1.0 % w/w *tert*-butyl alcohol to be used as a reference peak of 1.24 ppm.[44]

*[HDMBuA][OAc] (**1**).* ^1H NMR (700 MHz, D_2O) δ/ppm 14.04 (s, 1H) 2.98-2.96 (t, *J* = 7.8 Hz, 2H), 2.81 (s, 6H), 2.29 (s, 3H), 1.97-1.92 (p, *J* = 7.7 Hz, 2H), 1.78-1.72 (hx, *J* = 7.6, 7.4) 1.34 (t, *J* = 7.4). ^{13}C NMR (176 MHz, D_2O) δ 174.63, 58.24, 43.62, 28.34, 22.22, 20.56, 13.88.[39]

*[HTMEDA][OAc] (**2**).* ^{1}H NMR (700 MHz, DMSO-d6) δ/ppm 14.00 (s, 1H), 2.98 (s, 4H), 2.71 (t, 12H), 2.29 (s, 3H). ^{13}C NMR (176 MHz, D_2O) δ 174.47, 56.14, 44.90, 22.36. [39]

*[HDMEtA][OAc] (**3**).* ^{1}H NMR (700 MHz, D_2O) δ/ppm 10.02 (s, 2H), 4.00-3.98 (t, *J* = 5.0 Hz, 2H), 3.19-3.17 (t, *J* = 5.0 Hz, 2H), 2.88 (s, 6H), 2.11 (s, 3H). ^{13}C NMR (176 MHz, DMSO) δ 176.63, 59.89, 57.10, 43.50, 23.42. [39]

2.4 Solvatochromic parameters from UV-Visible Spectroscopy

The solvatochromic parameters α, β and π^* [28,29,32,35,45] were calculated based on the observed wavelength of maximum absorption, λ_{max}, of three solvatochromic dyes: 4-nitroaniline (NA), *N*,*N*-diethyl-4-nitroaniline (DE), and 2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (BD). The 2,6-dichloro derivative of the betaine dye was chosen because of its stability in strong hydrogen bond donating media, such as protic ionic liquids.[32,35,45]

The UV-Visible spectra in the region of 300 – 800 nm, with a 0.1 nm resolution, were recorded, at 298.15 K, using a Thermo Scientific Evolution 60S UV-Visible Spectrophotometer and quartz silica 1 cm path length cuvettes. A small quantity of a specific dye (c.a. 2-5 mg) was dissolved in 1 cm^3 of PIL, and was subsequently diluted to achieve a relative absorption value between 1 and 1.5. The wavelength was converted from nm to kKayser (10^3 cm^{-1}) for all necessary calculations. To calculate the solvatochromic parameters, the following equations were used: [28,29,32,35,45]

$$\alpha = [-0.182(8.48 - \lambda_{\max}\mathrm{BD}) - \ 0.72\pi^*] \quad (1)$$

$$\beta = \frac{(1.035\lambda_{max}\mathrm{DE}+2.64-\lambda_{max}\mathrm{NA})}{2.80} \quad (2)$$

$$\pi^* = 0.314(27.52 - \lambda_{max}\mathrm{DE}) \quad (3)$$

2.5 Density

Density measurements by the oscillating U-tube method were performed at 298.15 K, in an Anton-Parr DSA5000 apparatus. Calibration of the density meter was carried out by using freshly boiled de-ionized water with a known density of 0.997048±0.000001 g cm^{-3} at 298.15 K.[46] Care was taken to avoid the formation of air bubbles within the measurement chamber. The estimated accuracy of the results was 0.000001 g cm^{-3}. Density values were used to calculate the molar volumes of each PIL based on the corresponding molecular weights (Table 1).

Table 1: Experimental densities and molar volumes at 298.15 K of the three PILs under study

	1	**2**	**3**
ρ (g·mol$^{-1)}$	0.879215	0.91576	1.044627
M_w (g·mol^{-1})	161.245	176.26	149.19
V_m (cm^3·mol^{-1})	183.4	192.47	142.82

2.6 Viscosity

Viscosity measurements by the tuning-fork vibration method were performed using an A&D SV-10 Vibro Viscometer. The estimated accuracy of the determinations was 0.01 mPa·s. Temperature control to 298.15±0.01 K was achieved using a water circulator located on the floor so as not to disturb the measurements. The absolute viscosities of each of the three PILs were recorded once the instrument was brought to equilibrium and a stable value was obtained.

3 Results and discussion

3.1 Spectroscopic studies of equilibrium ionicity in PILs

In a recent study, Shen *et al.* proposed a new method to quantify the extent of proton transfer in the PIL *N*-propylammonium acetate based on ^{1}H NMR and ATR-IR spectroscopy data.[17] We were, however, unable to apply this approach to the PILs in this study.

The ^{1}H NMR characterization of the proton transfer extent relied on the investigation of how the chemical shift changes with slight modifications of the acid-amine ratio with subsequent regression analysis. There are two problems with this strategy. First, the signal corresponding to the labile protons in PIL **3** represent O–H of acetic acid, $N–H^+$ of protonated cations and O–H of both the neutral amine and protonated cations. This means there are two unknown chemical shifts which cannot be resolved by regression analysis. Second, the method assumes that the change in acid-amine composition does not influence the position of the proton transfer equilibrium in the neat PIL. This contradicts Le Chatelier's principle, where a change in concentration on one side of an equilibrium will result in a readjustment of the system to compensate it, and a new equilibrium is established.[47] As such, we are skeptical about the validity of this method for quantifying the equilibrium ionicity in a PIL.

For ATR-IR spectra, a calibration of the ratio in vibration peak areas for molecular and ionic species was constructed from mixtures of acetic acid and sodium acetate. The peak used to represent molecular (acetic acid) species was the C–OH stretch of the COOH group, which appeared in the region 1200-1300 cm^{-1}. We find that in this region each of the pure precursor amines exhibits a vibration mode, which is likely to be a C–N stretching mode. As such, the same calibration curve as used by Shen *et al.* cannot be applied to our systems. However, a different peak corresponding to neutral acetic acid can be observed in the attenuated total reflectance (ATR) infrared spectra of **1**, **2**, and **3** in the range 1500-1800cm^{-1}, as shown in Fig. 2.

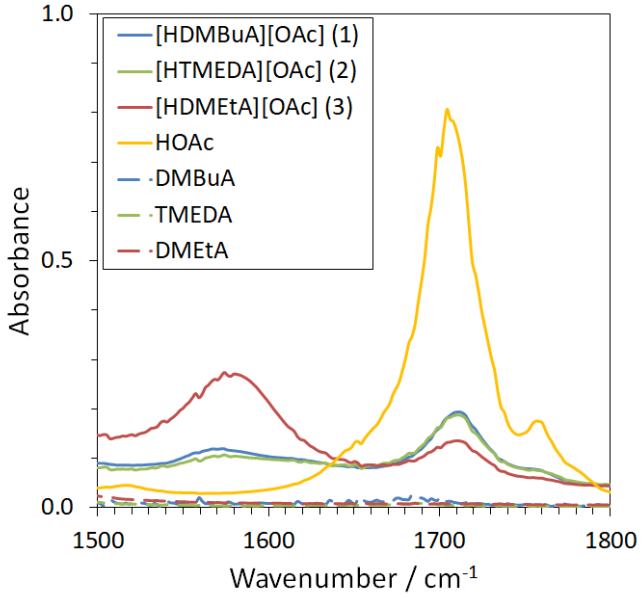

Fig. 2: ATR-Infrared spectra of the three PILs and of their corresponding precursors in the region of 1500-1800 cm^{-1}. The spectrum of **3** shows a significantly greater absorbance for the acetate species (~1570 cm^{-1}) than for the neutral species (~1710 cm^{-1}) when compared with the spectra of either **1** or **2**.

Peaks can be seen corresponding to the stretching mode of the C=O bond in neutral acetic acid, HOAc, at approximately 1710 cm^{-1}, and to the asymmetric stretching mode of the COO^- functional group of the acetate anion, $[OAc]^-$, at approximately 1570 cm^{-1}.[15,17] For reference, the infrared spectra of neat acetic acid and of the PILs precursor amines are also included. To qualitatively represent the extent of proton transfer, the ratio of the area of these two peaks, $A(OAc^-)/A(HOAc)$, has been calculated (Table 2). The obtained values suggest that the molar ratio of acetate to acetic acid and, consequently, the equilibrium ionicity, is greater for **3** than for **1** or **2**. While this observation is merely qualitative, a more in-depth study of how the IR-activity of these vibrational frequencies changes in each PIL would lead to potentially quantitative scrutiny from ATR-IR analysis of the ratio of these two peaks, and therefore the equilibrium ionicity.

In contrast, the equilibrium ionicity order given by the ΔpK_a values is **1** > **3** > **2** (Table 2). The greater ionic nature of **3** suggested by the ATR results may reflect a stabilization of the acetate ion through hydrogen bonding involving the hydroxyl group of the $[HDMEtA]^+$ cation, which is not possible in the cationic moieties of the other two PILs. Similar interactions have been suggested in the aprotic analogue of **3**, choline acetate.[48]

Table 2: The values of ΔpK_a and $A(OAc^-)/A(HOAc)$ of the three PILs as representative values of equilibrium ionicity.

	1	2	3
ΔpK_a [a]	5.26	4.38	4.87
$A(OAc^-)/A(HOAc)$ [b]	0.4026	0.3418	1.3709

[a] References [24–27]. [b] References [15,17]

Such function-specific factors influencing the ionic nature of PILs cannot, therefore, be rationalized through ΔpK_a alone.

The discrepancies between ΔpK_a and $A(OAc^-)/A(HOAc)$ are likely due to the different solvation environments of each measure. The ΔpK_a quantities are derived indirectly from aqueous dissociation constants, whereas the values of $A(OAc^-)/A(HOAc)$ are measured directly from the neat PIL medium. It has recently been shown that the dissociation constants of Brønsted acids in water and in the PIL ethylammonium nitrate vary slightly. A larger extent of proton dissociation is nevertheless observed when the PIL is used as solvent.[49]

3.2 Relating solvent properties of the PILs to apparent equilibrium ionicity

Table 3 shows that the α values for the three PILs are all similar, regardless of the cation functionality. PIL **3** may have been expected to exhibit a higher α value due to the presence of an additional hydrogen bond donor functional group but this was not observed. Such observation may be related to the fact that hydrogen bonding from $[HDMEtA]^+$ to $[OAc]^-$ reduces the hydrogen bonding donation (HBD) ability of **3** towards the solvatochromic probe. The obtained values are, however, comparable to those previously reported for acetate PILs,[45] which, in turn, are greater than those typical of similarly-sized short chain alcohols.[28] These high α values are indicative of the extensive hydrogen bonding network and amphiproticity that are common features of PILs.[50]

The β value for **3** is noticeably lower in comparison to the other two PILs. We surmise that this may be a result of hydrogen bonding between the hydroxyl group on the cation and the acetate anion, reducing the hydrogen bond acceptor capability of the anion. **2** exhibits the highest β value, which was expected due to the presence of an additional tertiary amino function on the cation. This may be anticipated to significantly alter the hydrogen bonding environment due to the formal equivalence of both amino functions in terms of their ability to interact with acetic acid. Interestingly, the increase of β by only 0.06 on going from **1** to **2** further suggests a small influence of the second amino function on the hydrogen bond acceptor ability of the PIL. It is likely that a low barrier hydrogen bond exists between the two nitrogen atoms, resulting in rapid proton exchange between these two centers on the (formally singly-charged) $[HTMEDA]^+$ cation.[51] The presence of this low barrier hydrogen bond will result in a lower proton affinity of the monoprotonated $[HTMEDA]^+$ cation compared to the unprotonated amine.

Table 3 Solvatochromic parameters for the three PILs in this study.

Parameter	1	2	3
α	0.95	0.98	0.95
β	0.95	1.01	0.69
π^*	0.69	0.69	0.94

Table 4: Molar volumes (V_m), enthalpies of vaporization, $\Delta_{vap}H^o_m$, cohesive energy densities (CED), viscosities (η) and Hildebrand parameter (δ_H) for the three PILs in this study.

	1	2	3
V_m ($cm^3 \cdot mol^{-1}$)	183.39	192.47	142.82
$\Delta_{vap}H^o_m$ ($kJ \cdot mol^{-1}$) [a]	107.9±1.7	116.9±0.4	119.2±0.7
CED ($J\ cm^{-3}$)	574.8	594.5	817.3
δ_H ($J^{0.5}\ cm^{-1.5}$)	24.0	24.4	28.6
η (mPa·s)	1.89	2.59	42.10
ΔpK_a [b]	5.26	4.38	4.86

[a] Reference [52]. [b] References [24–27,52].

In contrast, π^* is highest for **3**, with **2** and **1** showing identical values. This implies that stronger Keesom and Debye forces exist between the hydroxyl functionalized PIL and the DE dye than in the case of the alkyl or the tertiary amino functionalized PILs. With an increased ionic nature, it is to be expected that the permanent dipole moment will also increase. This is consistent with the equilibrium ionicity trend observed in the ATR infrared spectra (Fig. 2).

The δ_H parameter requires the cohesive energy density (CED) of each PIL to be known. This property can be determined from the standard molar enthalpy of vaporization, $\Delta_{vap}H^o_m$, and the molar volume, V_m, of each studied PIL according to:

$$\delta_H = \sqrt{\text{CED}} = \sqrt{\frac{\Delta_{vap}U^o_m}{V_m}} = \sqrt{\frac{\Delta_{vap}H^o_m - RT}{V_m}} \quad (1)$$

where $\Delta_{vap}U^o_m$ is the standard molar internal energy of vaporization, T is the absolute temperature (298.15 K) and R is the gas constant (8.3144598 $J\ mol^{-1} \cdot K^{-1}$).[53] The δ_H values used in this work are listed in Table 4. They rely on the V_m data here obtained from density measurements and on the previously determined $\Delta_{vap}H^o_m$ values,[52] also shown in Table 4.

A somewhat similar trend was observed for $\Delta_{vap}H^o_m$ and δ_H amongst the studied PILs: **3** displays the highest values for both properties, with **2** having a greater $\Delta_{vap}H^o_m$ but a comparable δ_H to **1**. While equivalent observations for $\Delta_{vap}H^o_m$ have been rationalized for variations within alkane, amine and alcohol series, through the formation of intermolecular hydrogen bonds,[54] the observed trends of δ_H (and corresponding CED) for the three PILs suggest significantly stronger solvent-solvent interactions in **3** than in **1** and **2**. The observed differences in δ_H correlate well with the ionic nature of the PILs as implied by their infrared spectra (Fig. 1) but not from their ΔpK_a values. Furthermore, the relative viscosities of these three PILs here determined were also found to correlate well with δ_H (Table 4) and the order of equilibrium ionicity inferred from ATR-IR data: the viscosity of **3** is far higher than those of the other two PILs, despite the fact that the corresponding ΔpK_a is lower than that of **1**.

Conclusions

To summarize, we have shown that the inclusion of a hydroxyl functional group on a PIL cation significantly increases its ionic nature when compared to a diamino or a non-functionalized (alkyl) cation. This cannot be rationalized from ΔpK_a considerations alone since the ionicity order **1** > **3** > **2** given by the ΔpK_a values differs from the order **3** > **1** ~ **2** deduced from the acetate to acetic acid molar ratio found in the ATR experiments. In contrast, the insights on the equilibrium ionicity of the PILs obtained from ATR spectroscopy correlate very well with the computed specific solvent-solute (β), non-specific solvent-solute (π^*) and solvent-solvent (δ_H) interaction parameters, as well as with the experimental viscosity (η). We have therefore shown that multiple factors contribute to the equilibrium ionicity of a PIL and that this complex property cannot be fully rationalized by a single relationship. Understanding the multiple factors underpinning the ionic character and properties of a PIL - and how they may be varied - is clearly a fundamental prerequisite before any attempt to rationally design such a material for a specific application can be made.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

J. E. S. J. Reid gratefully acknowledges financial support from the Engineering and Physical Sciences Research Council (EPSRC), through an industrial CASE award (EP/K504646/1). Financial support from Fundação para a Ciência e a Tecnologia (Portugal), through project UID/MULTI/00612/2013 and post-doctoral grants awarded to F. Agapito (SFRH/BPD/74195/2010) and C. E. S. Bernardes (SFRH/BPD/101505/2014) is also greatly appreciated.

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